

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08L 67/02	A1	(11) International Publication Number: WO 91/19767 (43) International Publication Date: 26 December 1991 (26.12.91)
(21) International Application Number: PCT/US91/03970 (22) International Filing Date: 11 June 1991 (11.06.91) (30) Priority data: 539,649 18 June 1990 (18.06.90) US 539,753 18 June 1990 (18.06.90) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: HOWE, King, Lau ; 414 Brentwood Drive, Wilmington, DE 19803 (US). (74) Agents: SHUE, Suzanne, E. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AT (European patent), BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published - <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: THERMOPLASTIC BLOW MOLDABLE POLYESTER COMPOSITIONS (57) Abstract Semi-crystalline blow moldable polyester compositions formed by melt blending a polyester, an ethylene copolymer containing epoxide groups, an ionomer obtained by neutralizing with Na ⁺ or K ⁺ and optionally a second polyester.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

THERMOPLASTIC BLOW MOLDABLE POLYESTER COMPOSITIONSBACKGROUND OF THE INVENTION

Polyesters that are semicrystalline,
5 particularly poly(ethylene terephthalate), PET, are
used extensively in many applications that require
good solvent resistance and good properties at
elevated temperatures. They are ordinarily processed
by injection molding, but there are many components of
10 automobiles and other systems wherein such parts are
hollow and to manufacture these by injection molding
is very difficult and expensive. Many such parts can
conceivably be made by blow molding provided the
polymer system has adequate melt strength and melt
15 viscosity and yields smooth high quality surfaces in
the blow molded parts. Unfortunately, polyesters
commercially available for injection molding and
extrusion have melt viscosities which are too low to
make them suitable for extrusion blow molding. It
20 would be desirable to have blow moldable polyester
compositions which provide moldings having smooth
surfaces made from commercial injection moldable and
extrusion grades of polyesters.

The addition of conventional di- and
25 polyepoxides and, more recently, the addition of
ethylene copolymers containing glycidyl groups have
been suggested for increasing the melt strength and
viscosity of polyesters, but are not suitable for blow
molding large objects having smooth surfaces and
30 having complex cross-sections such as automobile
parts.

Further improvements in melt strength and
melt viscosity have been provided by compositions
which in addition to the ethylene copolymers
35 containing glycidyl groups use small amounts of

catalytic cations which may be introduced in the form of a zinc ionomer. Unfortunately it has been found that these catalyzed compositions may form small lumps when the compositions are exposed to processing temperatures for an extended period of time. Such prolonged exposure is not unusual in commercial blow molding operations where a substantial proportion of the resin must be recycled as regrinds. The presence of these lumps results in molded objects having surface blemishes or surface irregularities.

Thus a need still exists for polyester compositions, particularly for PET-based compositions, which have sufficient melt strength and viscosity to permit extrusion blow molding of large and complex objects which at the same time exhibit uniform, smooth surfaces.

BACKGROUND ART

U.S. Patent 4,659,757, granted April 21, 1987 to Okamoto et al., discloses poly(ethylene terephthalate) (PET) molding compositions yielding impact resistant articles prepared by melt blending PET with 3 to 60 parts of a second polyester selected from the group consisting of (1) copolymers of ethylene glycol, terephthalic acid and aliphatic dicarboxylic acids containing at least 12 carbon atoms (2) copolymers of ethylene glycol, terephthalic acid and a poly(alkylene oxide) glycol, and (3) polyarylates. In addition the compositions must also contain (i) a nucleating agent selected from the group of finely divided inorganic nucleating agents, a metal salt of an organic carboxylic acid and an ionomer, (ii) a polyolefin to which has been grafted an olefin having carboxyl or anhydride groups, (iii) an olefin copolymer containing units derived from glycidyl (meth)acrylate and optionally units derived from vinyl

acetate as a third monomer and (iv) an ester-based plasticizer. As claimed, the compositions must contain the second polyester and each of ingredients (i), (ii), (iii) and (iv).

5 U.S.P. No. 4,912,167, granted March 27, 1990 to Deyrup et al and U.S.P 4,914,156, granted April 3, 1990 to Howe, disclose compositions which are blow moldable PET or poly(butylene terephthalate), PBT, containing an epoxide group-containing copolymer and a
10 source of catalytic metal cations which source could be a small amount of a zinc ionomer, for example. The patents disclose olefin copolymers and acrylate copolymers containing epoxide groups, but prefers the olefin copolymers. The examples of the reference
15 demonstrate that sodium ionomers are ineffective in providing blow moldability when used at the same concentration at which zinc ionomers are effective.

U.S. Patent 4,783,980, granted January 28, 1988 to Deyrup discloses toughened thermoplastic
20 polyester compositions prepared by melt blending at high shear 3-40 weight percent of an ethylene copolymer containing epoxide groups and 10-40 weight percent of units derived from a C₂-C₈ alkyl (meth)acrylate. A variety of optional ingredients may
25 be added including plasticizers, poly(alkylene oxide) segments and crystallization promoters. As crystallization promoters one can use salts of hydrocarbon acids containing 7 to 54 carbon atoms or salts of ionomeric polymers. Example 1 discloses a
30 single poly(ethylene terephthalate) composition which contains 3.8 weight percent of a sodium ionomer of an ethylene/methacrylic acid copolymer added as a crystallization promoter.

U.S. Patent 4,034,013 granted July 5, 1977
35 to Lane discloses that the notched impact strength and

melt strength of PET and PBT are improved by incorporating small particles of a core-shell polymer wherein the core is a rubbery acrylate copolymer and the shell is a more rigid acrylate or styrene
5 copolymer containing epoxide groups.

Japanese Patent Publication 59-184251, published October 19, 1984 discloses that polyether ester block copolymers (100 parts) derived essentially from terephthalic acid, 1,4-butanediol and a
10 poly(alkylene oxide) glycol when melt blended with 1-25 parts of an ionomer resin and 1-25 parts of an olefin copolymer containing epoxide groups form compositions having sufficiently high melt tension to permit extrusion blow molding. The compositions are
15 further characterized as exhibiting good elastic recovery and softness.

U.S. Patent 4,246,378, granted January 20, 1981 to Kometani et al discloses the addition of ethylene copolymers containing glycidyl groups for
20 increasing the melt strength and viscosity of polyesters.

SUMMARY OF THE INVENTION

The present invention provides polyester compositions which are suitable for extrusion blow
25 molding large objects having smooth surfaces. The compositions are based on injection molding and extrusion grades of PET.

More specifically, the compositions of the present invention are semi-crystalline blow moldable
30 compositions comprising melt blends consisting essentially of the following ingredients:

a) 62-88 weight percent of at least one PET selected from the group consisting of branched PET having an inherent viscosity of at least about 0.60
35 dl/g and a mixture of the branched PET and a linear

PET having an inherent viscosity of at least about 0.65 dl/g, the mixture containing up to 90 weight percent of the linear PET or at least one poly(butylene terephthalate) (PBT) having an inherent viscosity of at least about 0.8 dl/g,

5 b) 10-30 weight percent of at least one ethylene copolymer, E/X/Y, wherein E is at least 50 weight percent of units derived from ethylene, X is 2-10 weight percent of units derived from glycidyl (meth)acrylate and Y is 0-40 weight percent of units derived from a C₁-C₆ alkyl (meth)acrylate, and

10 c) 2-8 weight percent of at least one ionomer obtained by neutralizing with Na⁺ or K⁺ at least about 40 percent of the carboxyl groups in an ethylene copolymer which contains about 9-20 weight percent of units derived from (meth)acrylic acid and 0-35 weight percent of units derived from C₁-C₆ alkyl (meth)acrylate.

Optionally, component d), a second polyester other than PET, may be added in the amount of 2-6 parts per 100 parts (pph) by weight of components a), b) and c), which second polyester assists in the processing of the compositions. The second polyester is selected from the group consisting of (1) polyesters of C₃-C₁₀ α, ω-diols and aromatic dicarboxylic acids, (2) polyarylates and (3) copolyetherester block copolymers.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to semi-crystalline blow moldable polyester compositions which possess high melt strengths and melt viscosities as well as yielding high quality smooth surface appearance on the blow molded parts.

More specifically, the compositions of the present invention are semi-crystalline blow moldable

compositions comprising melt blends consisting essentially of the following ingredients:

- a) 62-88 weight percent of at least one PET selected from the group consisting of branched PET having an inherent viscosity of at least about 0.60 dl/g and a mixture of the branched PET with a linear PET having an inherent viscosity of at least about 0.65 dl/g, the mixture containing up to 90 weight percent of the linear PET or at least one PBT having an inherent viscosity of at least about 0.8 dl/g,
- b) 10-30 weight percent of at least one ethylene copolymer, E/X/Y, wherein E is at least 50 weight percent of units derived from ethylene, X is 2-10 weight percent of units derived from glycidyl (meth)acrylate and Y is 0-40 weight percent of units derived from a C₁-C₆ alkyl (meth)acrylate, and
- (c) 2-8 weight percent of at least one ionomer obtained by neutralizing with Na⁺ or K⁺ at least about 40 percent of the carboxyl groups in an ethylene copolymer which contains about 9-20 weight percent of units derived from (meth)acrylic acid and 0-35 weight percent of units derived from C₁-C₆ alkyl (meth)acrylate.

The weight percentages given for each of components a), b) and c) are based on the total of these components only.

In the above description, and throughout this application the description "(meth)acrylate" is meant to include both "acrylate" and "methacrylate."

Optionally, component d), a second polyester other than PET, may be added in the amount of 2-6 pph by weight of components a), b) and c), which second polyester assists in the processing of the compositions. The second polyester is selected from the group consisting of (1) polyesters of C₃-C₁₀

α, ω -diols and aromatic dicarboxylic acids, (2) polyarylates and (3) copolyetherester block copolymers.

5 Preferred compositions of the present invention are semi-crystalline blow moldable compositions comprising melt blends consisting essentially of the following ingredients:

10 a) 69-82 weight percent of at least one PET selected from the group consisting of branched PET having an inherent viscosity of at least about 0.60 dl/g and a mixture of the branched PET with a linear PET having an inherent viscosity of at least about 0.65 dl/g, the mixture containing up to 80 weight percent of the linear PET or at least one PBT having an inherent viscosity of at least about 0.8 dl/g,

15 b) 15-25 weight percent of at least one ethylene copolymer, E/X/Y, wherein E is at least 57 weight percent of units derived from ethylene, X is 4-8 weight percent of units derived from glycidyl (meth)acrylate and Y is 10-35 weight percent of units derived from a C₁-C₆ alkyl (meth)acrylate, and

20 (c) 3-6 weight percent of at least one ionomer obtained by neutralizing with Na⁺ or K⁺ at least about 40 percent of the carboxyl groups in an ethylene copolymer which contains about 9-20 weight percent of units derived from (meth)acrylic acid and 0-35 weight percent of units derived from C₁-C₆ alkyl (meth)acrylate.

25 Optionally, component d), a second polyester other than PET, may be added in the amount of 3-5 parts per 100 parts by weight of components a), b) and c), which second polyester assists in the processing of certain compositions. The second polyester is selected from the group consisting of (1) polyesters of C₃-C₁₀ α, ω -diols and aromatic dicarboxylic acids,

35

(2) polyarylates and (3) copolyetherester block copolymers.

Component a) is a polyester selected from the group consisting of branched poly(ethylene terephthalate) (PET) having an inherent viscosity of at least 0.60 dl/g, mixtures of the branched PET with up to 90 weight percent of linear PET having an inherent viscosity of at least about 0.65 dl/g and PBT having an inherent viscosity of 0,8 dl/g.

Linear PET is a well established commercial product which is normally made by esterification of terephthalic acid with ethylene glycol followed by polycondensation. PET having an inherent viscosity of about 0.65 dl/g may be made by polycondensation in the melt. PET having inherent viscosities of about 1.0 dl/g are usually prepared by subsequent solid phase polycondensation of lower molecular weight PET first prepared by melt condensation. Recycled PET bottle resin represents a source of relatively inexpensive linear PET which with proper recycling of PET bottles will be available in very substantial amounts. The PET used for bottles normally contains a minor amount, about 2% by weight, of a second glycol such as diethylene glycol, the presence of which facilitates the manufacture of oriented PET bottles; and normally has an inherent viscosity of at least 0.65 dl/g and preferably has an inherent viscosity of about 0.7-0.72 dl/g. The presence of the second glycol monomer does not adversely affect the use of recycled PET resin in the present invention.

Branched PET can be made by substantially the same processes as are used for linear PET with the exception that a minor amount of a tri- or higher functionality polyol or polyacid monomer is added to the polymerization. Trifunctional acids are usually

preferred and of these, trimellitic anhydride or tri-lower alkyl esters of trimellitic acid are especially preferred. From about 0.2-1.0 mole of trifunctional monomer per 100 moles of terephthalic acid can be used with 0.4 to 0.7 moles being preferred.

Branched PET containing preferred amounts of branching agent; i.e., 0.4 to 0.7 moles of branching agent per 100 moles of terephthalic acid, are useful for preparing compositions of this invention which can be used for forming very large articles by extrusion blow molding. When blends of branched and linear PET are used, the higher the inherent viscosity of the linear PET, the smaller may be the proportion by weight of branched PET in the blends. The concentration of branching agent in the branched PET is also important in that a lesser amount of branched PET containing a higher level of branching agent is required than is a branched PET containing lower levels of branching agent. Compositions prepared from mixtures containing 10-60 weight percent branched PET, preferably 20-50 weight percent, having the preferred concentration of branching agent with recycled PET bottle resin, which normally has an inherent viscosity of about 0.7 dl/g, are very economical and highly useful for extrusion blow molding.

Branched PET has a higher melt viscosity and greater melt strength than does linear PET having the same inherent viscosity. Because of these properties, branched PET having relatively low inherent viscosity is useful either alone or in admixture with linear PET in preparing the compositions of this invention. The use of branched PET alone or in blends with linear PET having a relatively low inherent viscosity yields compositions which are versatile in terms of the size

and complexity of the articles which can be blow molded from them. For economic reasons, blends of branched PET with recycled PET bottle resin are of particular interest.

5 Moreover, component a) may be poly(butylene terephthalate) (PBT) having an inherent viscosity of at least about 0.8 dl/g. PBT is a well-known commercial product. It is normally made by transesterification of dimethyl terephthalate with
10 excess 1,4-butanediol followed by polycondensation. It is also possible to start with terephthalic acid and butanediol. In order to obtain resins having inherent viscosities of at least about 0.8 dl/g it is necessary to use a continuous finisher when melt
15 condensation is used exclusively. With batch finishing, melt condensation followed by solid phase condensation is generally required to obtain the desired inherent viscosities.

 Compositions prepared from PBT having
20 inherent viscosities near the minimum value stated above are generally suitable for extrusion blow molding of articles requiring the use of parisons having a length of up to about 30.5 cm (one foot). To prepare compositions which can be used to form larger
25 parisons, resins having inhereents above about 0.8 dl/g are preferred.

 Component b) is an ethylene copolymer, E/X/Y, where E is at least 50 weight percent of units derived from ethylene, X is 2-10 weight percent of
30 units derived from glycidyl (meth)acrylate and Y is about 0-40 weight percent of units derived from C₁-C₆ alkyl (meth)acrylate. Thus, component b may be a dipolymer of ethylene and glycidyl (meth)acrylate. More preferred are terpolymers containing up to 40
35 weight percent of units derived from meth(acrylate)

lower alkyl esters of which n-butyl acrylate is preferred. Most preferred are terpolymers of ethylene containing 10-35 weight percent of n-butyl acrylate and 4-8 weight percent of glycidyl methacrylate.

5 Component b) is used in amounts of 10-30 weight percent, and more preferably 15-25 weight percent based on the total weight of components a), b), and c). Since components b) and c) each contribute to the blow moldability of the instant
10 compositions by increasing melt viscosity, melt strength and die swell, the preferred amount of component b) used within the aforementioned ranges is partly dependent on the level of component c). The epoxide content of component b) is another factor
15 which affects the amount of component b) used. In general, the greater the epoxide content of component b), the less of component b) will be required. Finally, consideration must be given to the proportion of branched PET used as well as its concentration of
20 branching agent.

 Component c) is an ionomer obtained by neutralizing with Na^+ or K^+ , provided by a basic sodium or potassium compound, at least about 40 percent of the carboxyl groups contained in an
25 ethylene copolymer containing about 9-20 weight percent of units derived from (meth)acrylic acid. Optionally these ionomers may contain up to about 35 weight percent of units derived from C_1 - C_6 alkyl (meth)acrylate. A preferred termonomer is n-butyl
30 acrylate. Component c) is used in amounts of 2-8 weight percent, preferably 3-6 weight percent based on the total weight of components a), b), and c). Since component c) contributes to the blow moldability of the compositions of this invention, the preferred
35 amount of component c) used depends at least in part

on the amount of component b) present in a given composition. In addition, component c) improves the stability of the molten composition during processing which in turn permits extrusion of smooth parisons and
5 forming molded articles with smooth surfaces.

As noted above, each of components b) and c) contributes to the blow moldability of the compositions of this invention. In general, increasing the concentration of either of the
10 components within the ranges specified will raise the melt viscosity of a given blow molding composition. While blow moldability is more than a function of melt viscosity, for guidance it should be noted that compositions having melt viscosities at about 270°C
15 for PET and 260°C for PBT of at least about 10,000 to 15,000 Pa sec at 1 sec⁻¹ are usually suitable for forming articles requiring a parison of up to about 61 cm (2 feet) in length and compositions having melt viscosities at the above temperature of at least about
20 20,000 to 30,000 Pa sec at 1 sec⁻¹ are usually suitable for forming articles requiring a parison greater than 61 cm in length. The melt rheology of the compositions of the present invention makes them suitable for thermoforming applications.

25 Reference to the Samples contained below will assist one in selecting amounts of components b) and c) which will yield a composition suitable for a given molding application.

As stated above, the addition of a minor
30 amount of a polyester other than branched and/or linear PET may assist in the processing of certain compositions based on PET. Compositions melting near 250°C or above generally exhibit melt viscosities which diminish rapidly with increasing temperatures in
35 the range used for blow molding. The ratio of the

melt viscosity at 270°C to the melt viscosity at 280°C may approach 10 for some compositions. Because of this extreme sensitivity of the melt viscosity to temperature, minor fluctuations in temperature on the low side result in excessive torque within the extruder of the blow molding machine while conversely, temperatures on the high side cause the melt to be too fluid to form a stable parison. Such compositions can only be blow molded satisfactorily in equipment where excellent temperature control is possible. By adding a minor amount of a second polyester, such sensitive compositions are converted to materials which can be readily processed in any conventional extrusion blow molding machine. The addition of a second polyester is usually not required for compositions of the present invention containing substantial amounts of recycled bottle PET because such PET already contains a second monomer which lowers the melting point of the composition and improves processibility.

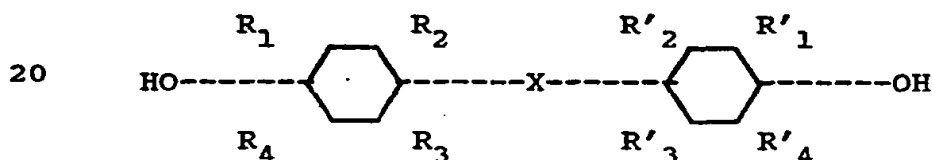
In essence, any polyester based on a diol other than ethylene glycol and/or based on a diacid other than terephthalic acid can be used to improve the processing of compositions which exhibit the problems just discussed. Polyesters based on aromatic diacids are preferred because compositions modified with aliphatic polyesters may exhibit decreased hydrolytic stability. Three classes of polyesters have been found to be particularly useful for the modification of temperature sensitive compositions. They are as follows:

1. Polyesters of C_3-C_{10} *aliphatic* diols and an aromatic dicarboxylic acid;
2. Polyarylates of dihydric phenols and an aromatic dicarboxylic acid, and

3. Copolyetherester block copolymers derived from a low molecular weight diol, a polyether glycol and an aromatic dicarboxylic acid.

5 The polyesters of class 1 are close relatives of PET and can be prepared substantially by the same condensation procedures used to make PET. *o,w*-diols are preferred. Preferred dicarboxylic acids are the three isomeric phthalic acids, but
 10 substituted phthalic acids and acids such as 1,5-, 2,6- and 1,4-naphthalene dicarboxylic acid are also useful. The preferred polyester of class 1 is PBT.

The polyarylates of class 2 are aromatic polyesters derived from one or more dihydric phenols and one or more aromatic dicarboxylic acids. The
 15 dihydric phenol is preferably a bisphenol as described in U.S. Patent 4,187,358 having the structure:



wherein $-X-$ is selected from the group
 25 consisting of nothing; i.e., a covalent bond, $-O-$, $-S-$, $-SO_2-$, $-SO-$, $-CO-$, an alkylene group containing 1 to 5 carbon atoms and an alkylidene group containing 2 to 7 carbon atoms, and R_1 , R_2 , R_3 , R_4 , R'_1 , R'_2 , R'_3 , and R'_4 , may be the same or different, and each is
 30 selected from the group consisting of a hydrogen atom, a chlorine atom, a bromine atom and an alkyl group containing 1 to 5 carbon atoms, and/or a functional derivative thereof. 2,2'-Bis(4-hydroxyphenyl)propane is most preferred.

35 Additionally, up to 40 mole percent of mononuclear dihydric phenols may be used in

combination with the bisphenols. Representative are hydroquinone and resorcinol and substituted derivatives thereof containing one to four substituents selected from the group consisting of chlorine, bromine and lower alkyl.

Preferably, a mixture of 90 to 0 mole percent of terephthalic acid and/or the functional derivatives thereof and 10 to 100 mole percent of isophthalic acid and/or its functional derivatives is used as the acid component to be reacted with the bisphenol to prepare the polyarylate. Preparative methods for polyarylates are described in detail in U.S. Patent Nos. 3,884,990, 3,946,091, 4,052,481 and 4,485,230.

Preferred polyarylates for use in the compositions of this invention are derived from isophthalic acid optionally containing up to 30 weight percent terephthalic acid and 2,2'-bis(4-hydroxyphenyl)propane.

The copolyetherester block copolymers of class 3 consist essentially of 15-95 weight percent of short chain ester units which are derived from a low molecular weight diol and an aromatic dicarboxylic acid and 5-85 weight percent of long chain ester units which are derived from a poly(alkylene oxide) glycol having a number average molecular weight of 400-6000 and an aromatic dicarboxylic acid. These polymers are readily prepared by substantially the same procedures useful for preparing PET, with the exception of adding a poly(alkylene oxide) glycol to the reaction mass. Polymers derived from terephthalic acid (optionally containing some isophthalic acid), butanediol and a poly(alkylene oxide) glycol selected from the group consisting of poly(tetramethylene oxide) glycol, poly(1,2-propylene oxide) glycol and

ethylene oxide-capped poly(1,2-propylene oxide) glycol are readily available as commercial products.

Of the three classes of polyesters, those of class 1 are preferred with poly(butylene terephthalate) being especially preferred when molded articles having high flexural modulus are desired. It should be noted that the polyesters of class 3 which are known to be elastomers reduce the rigidity of the compositions of this invention and yield articles having outstanding impact resistance.

When the compositions are modified by the addition of a second polyester, the second polyester should be used in amounts of 2-6 parts by weight, preferably 3-5 parts by weight, based on 100 parts of the sum of components a), b) and c). Note that the sum of the percentages of a), b) and c) equals 100 weight percent and the amount of the second polyester, being an optional component, is in addition to the weight of the basic composition.

The compositions of the present invention may contain minor amounts of a variety of additives which are frequently used in plastics. Such additives include antioxidants, UV stabilizers, dyes, pigments, flame retardants, fibrillatable fluoropolymers and fillers. The use of reinforcing fillers such as chopped glass fibers and acicular calcium metasilicate permits the preparation of moldings which exhibit exceptional rigidity. Reinforcing fillers may be used in amounts of up to about 40 parts by weight based on 100 parts of the total of components a), b) and c) which three ingredients total 100%. In other words, up to about 40 parts by weight of filler can be used for 100 parts by weight of components a), b) and c). The presence of reinforcing fillers generally raises the melt viscosity of the compositions of this

invention. If significant amounts of reinforcing fillers are used it may be necessary to either (1) decrease the amounts within the limits specified herein of components b and c each of which enhances melt viscosity; or (2) employ a PBT with an inherent viscosity approaching the lower limit of 0,8 dl/g or PET or PET mixture [component a)] with a lower melt viscosity. For instance, with 20 parts of acicular calcium silicate, compositions based on branched PET having an inherent viscosity of 0.65 dl/g are so viscous that they may overheat in the extruder. This problem may be remedied by replacing part of the branched PET with linear PET having an inherent viscosity of about 0.65 to 0.7 dl/g. Because of their potentially low cost, filled compositions based largely on recycled bottle PET are of particular interest for blow molded articles exhibiting exceptional rigidity.

In the following samples the various samples were prepared by melt blending the indicated ingredients, by extrusion in a 28 or 57 mm twin screw extruder.

For Table VI and VIII below the ingredients of the compositions, namely components a, b and c, were added to the rear of the extruder. For illustration, the feed rates for Sample 8-1 are as follows:

Component a: 53.0 kgs/hr
Component b: 12.3 kgs/hr
Additives A and B: 726 gms/hr

The ingredients were blended on a Werner and Pfleiderer bilobal twin screw extruder having a diameter of 57 mm and a length to diameter ratio of 37. The screw used was a general purpose screw with vacuum capability consisting of conveying elements to

convey the feed material from the feed zone to a melting zone in which the material was compressed and melting begins. A section of "kneading blocks" followed by "reverse elements" next provides high shear and pressure to further the melting and mixing process. The reverse elements serve also to provide a melt seal following which the melt is decompressed in the section under vacuum. Following the vacuum zone, introduced via a side feeder at the rate of 6.54 kg/hour was a mixture obtained by dry blending components c) and components d) at a ratio of 9.6 to 4.8, respectively. Also introduced via the side feeder was Additive C at the rate of 18.2 kg/hr. After the side feeder, the screw recompresses the melt and passes it through kneading blocks and reverse elements which also serve as a vacuum seal for a second vacuum zone. Then the melt is recompressed and mixed as it passes through the end of the extruder and out the die.

Representative extrusion conditions for the compositions shown in Table VIII are:

	Setting Zone 1 (°C)	Setting Zone 2 (°C)	Setting Zone 3 (°C)	Setting Zone 4 (°C)	Setting Zone 5-10 (°C)	Setting Die (°C)
25	260	260	260	260	260	260
	Sample	Screw Speed (rpm)	Extru. Rate Kg/hr	Melt Temp (°C)		
30	8 - 1	225	90.8	326		

The product was extruded at a rate of 90.8 kgs/hour through a six hole die. Temperature of the melt exiting the extruder die was measured as the melt

temperature. Melt strands exiting the extruder were quenched in water and cut into pellets. The pelletized product was dried at 100-105°C in a circulating air drier equipped with dehumidifier.

5 Representative extrusion conditions for the compositions shown in Table VI are:

	Setting Zone 1 Temp (°C)	Setting Zone 2 Temp (°C)	Setting Zone 3 Temp (°C)	Setting Zone 4 Temp (°C)	Setting Zone 5-10 Temp (°C)	Setting Die Temp (°C)
10	270	270	270	270	270	270

	Sample	Screw Speed (rpm)	Extru. Rate Kg/hr	Melt Temp (°C)
15	6 - 1	175	68.1	326
	6 - 2	175	68.1	316
	6 - 3	175	68.1	323

20 For the remaining Samples in Table VI, the amounts and proportions of the various components can be calculated from the information in Table VI.

For Tables VII below the ingredients of the compositions were placed in a polyethylene bag and tumbled to mix. The resulting dry blend was melt
 25 blended on a Werner and Pfliederer twin-screw extruder having a diameter of 28mm and a length to diameter ratio of 27.5. The screw used is a general purpose screw with vacuum capability consisting of
 30 conveying elements to convey the feed material from the feed zone to a melting zone in which the material is compressed and melting begins. A section of "kneading blocks" followed by "reverse elements" next provides high shear and pressure to further the
 35 melting and mixing processes. The reverse elements

serve also to provide a melt seal following which the melt is decompressed in the section under vacuum.

Following the vacuum zone, the screw recompresses the melt and passes it through kneading blocks and reverse elements which also serve as a vacuum seal for this side of the vacuum zone. The melt is then further compressed and mixed as it passes through the end of the extruder and out the die.

Representative extrusion conditions for the compositions shown in Table VII are:

	Setting Zone 1 (°C)	Setting Zone 2 (°C)	Setting Zone 3 (°C)	Setting Zone 4 (°C)	Setting Zone 5 (°C)	Setting Die (°C)
15	260	260	260	260	260	260

	<u>Sample</u>	<u>Screw Speed (rpm)</u>	<u>Extru. Rate Kg/hr</u>	<u>Melt Temp (°C)</u>
20	7 - 1	175	9.3	305
	7 - 2	175	8.2	313
	7 - 3	175	9.4	297
	7 - 4	175	7.8	312

Temperatures of the melt exiting the extruder die were measured and reported above. The melt strand exiting the extruder was quenched in water and cut into pellets. The pelletized product was dried in a vacuum oven set at 120°C and purged with a slight nitrogen sweep overnight. For example, Sample 7-1 had a melt viscosity, measured using a Kayeness viscometer at 270°C of 30045 Pa sec at 1 sec⁻¹, and 968 Pa sec at 1000 sec⁻¹.

For illustration, the feed rates for Sample 9-1 in Table IX are as follows:

Component a): 40.8 kg/hr.
Component b): 11.6 kg/hr.

Additive B: 136 gm/hr.

The ingredients for Sample 9-1 were blended on a Werner and Pfleiderer bilobal twin screw extruder having a diameter of 57mm and a length to diameter ratio of 37. The screw used was a general purpose screw with vacuum capability consisting of conveying elements to convey the feed material from the feed zone to a melting zone in which the material was compressed and melting begins. A section of "kneading blocks" followed by "reverse elements" next provides high shear and pressure to further the melting and mixing process. The reverse elements serve also to provide a melt seal following which the melt is decompressed in the section under vacuum. Following the vacuum zone, introduced via a side feeder, for Sample 9-1 in Table IX at the rate of 15.47 kg/hour was a mixture obtained by dry blending 125.9 kg of component a) and 28.99 kg of component c). After the side feeder, the screw recompresses the melt and passes it through kneading blocks and reverse elements which also serve as a vacuum seal for a second vacuum zone. Then the melt is recompressed and mixed as it passes through the end of the extruder and out the die.

For the remaining Samples in Tables X, the amounts and proportions of the various components can be calculated from the information in Tables X.

22

Representative extrusion conditions for the compositions shown in Table IX are:

5	<u>Setting Zone 1 (°C)</u>	<u>Setting Zone 2 (°C)</u>	<u>Setting Zone 3 (°C)</u>	<u>Setting Zone 4 (°C)</u>	<u>Setting Zone 5-10 (°C)</u>	<u>Setting Die (°C)</u>
	240	240	240	240	230	250

10	<u>Sample</u>	<u>Screw Speed (rpm)</u>	<u>Extru. Rate Kg/hr</u>	<u>Melt Temp (°C)</u>
	9 - 1	200	68.1	322
	9 - 2	200	68.1	322

Representative extrusion conditions for the compositions shown in Table X are:

20	<u>Setting Zone 1 Temp (°C)</u>	<u>Setting Zone 2 Temp (°C)</u>	<u>Setting Zone 3 Temp (°C)</u>	<u>Setting Zone 4 Temp (°C)</u>	<u>Setting Zone 5-10 Temp (°C)</u>	<u>Setting Die Temp (°C)</u>
	240	240	240	240	230	250

25	<u>Sample</u>	<u>Screw Speed (rpm)</u>	<u>Extru. Rate Kg/hr</u>	<u>Melt Temp (°C)</u>
	10 - 1	150	68.1	289
	10 - 1A	200	68.1	308
	10 - 2	150	68.1	300
	10 - 2A	200	68.1	309
	10 - 3	150	68.1	294
	10 - 4	150	68.1	296
30	10 - 5	150	68.1	289
	10 - 6	150	68.1	289
	10 - 7	150	68.1	292
	10 - 8	150	68.1	290
	10 - 9	150	68.1	-
	10 - 9A	200	68.1	305
	10 - 10	150	68.1	-

35

The product was extruded at a rate of 68 kgs/hour through a six hole die. Temperature of the melt exiting the extruder die was measured as the melt temperature. Melt strands exiting the extruder
5 were quenched in water and cut into pellets. The pelletized product was dried at 95°C in a circulating air drier equipped with dehumidifier.

For Table XI the ingredients of the compositions were placed in a polyethylene bag and
10 tumbled to mix.

The resulting dry blend was melt blended on a Werner and Pfleiderer twin-screw extruder having a diameter of 28mm and a length to diameter ratio of 27.5. The screw used is a general purpose screw with
15 vacuum capability consisting of conveying elements to convey the feed materials from the feed zone to a melting zone in which the material is compressed and melting begins. A section of "kneading blocks" followed by "reverse elements" next provides high
20 shear and pressure to further the melting and mixing processes. The reverse elements serve also to provide a melt seal following which the melt is decompressed in the section under vacuum. Following the vacuum zone, the screw recompresses the melt and passes it
25 through kneading blocks and reverse elements which also serve as a vacuum seal for this side of the vacuum zone. The melt is then further compressed and mixed as it passes through the end of the extruder and out the die.

30

35

Representative extrusion conditions for the compositions shown in Table XI for each sample are:

Setting Zone 1 (°C)	Setting Zone 2 (°C)	Setting Zone 3 (°C)	Setting Zone 4 (°C)	Setting Zone 5 (°C)	Setting Die (°C)
260	260	260	260	260	260

<u>Sample</u>	<u>Screw Speed (rpm)</u>	<u>Extru. Rate Kg/hr</u>	<u>Melt Temp (°C)</u>
11 - 1	150	7.4	305
11 - 2	150	7.5	307
11 - 3	150	7.9	298
11 - 4	150	8.0	304
11 - 5	150	7.4	299
11 - 6	150	7.4	298
11 - 7	150	7.5	297

Temperatures of the melt exiting the extruder die were measured and reported above. The melt strand exiting the extruder was quenched in water and cut into pellets. The pelletized product was dried in a vacuum oven, set at 95°C and purged with a slight nitrogen sweep overnight. For example, Sample 11-2 had a melt viscosity, measured using a Kayeness viscometer at 260°C of 23000 Pa sec at 1 sec-1, and 1200 Pa sec at 1000 sec-1.

The dried resins for each extruded sample from Tables VI and VII were blow molded using a Rocheleau molding machine equipped with a single-screw extruder. The screw had a 3.81 cm diameter, a length to diameter ratio of 20 and a compression ratio of 2 to 1. Samples marked with dashes denote that the particular sample was not blow molded.

25

Representative blow molding temperature profiles used to produce the blow mold parts that appear on Table VI are:

5	<u>Setting Feed Zone (°C)</u>	<u>Setting Transition Zone (°C)</u>	<u>Setting Metering Zone (°C)</u>	<u>Setting Die Zone (°C)</u>
10	270	270	265	260
	<u>Sample</u>	<u>Screw Speed (rpm)</u>	<u>Mold Geometry</u>	
15	6 - 1	54	Bottle	
	6 - 2	73	Bottle	
	6 - 3	110	Bottle	

Representative blow molding conditions and temperature profiles used to produce the blow molded parts that appear in Table VII are:

20	<u>Setting Feed Zone (°C)</u>	<u>Setting Transition Zone (°C)</u>	<u>Setting Metering Zone (°C)</u>	<u>Setting Die Zone (°C)</u>
25	260	260	260	250
	<u>Sample</u>	<u>Screw Speed (rpm)</u>	<u>Mold Geometry</u>	
30	7 - 1	77	Bottle	
	7 - 2	40	Bottle	
	7 - 3	105	Bottle	
	7 - 4	47	Bottle	

The resins for each Sample in the Tables above were extruded at the designated screw speed through the die to produce a parison. Upon closing

the molded, the part is blown with air at about 400 MPa. The blown part is cooled in the mold under pressure and ejected. The mold geometry of the bottles are 22.5 cm high and 7.5 cm diameter; and the spoiler has dimensions of 136 cm long, 9 cm wide and 1.5 cm thick.

Blow molded automobile spoilers, were also produced from the compositions of Table VIII. The procedure and conditions used for blow molding the spoiler are as follows:

The dried resin product was blow molded using a Sterling blow molding machine equipped with a 819 cm diameter barrier type screw with a length to diameter ratio of 24:1 and an accumulator of the first-in-first-out design with a capacity of 6.8 kg. The extruder barrel of the blow molding machine was heated and the temperature regulated at 260°C, 260°C, 255°C and 255°C for each of the four temperature zones, respectively. The three zones of the accumulator were set at 263°C. The extruder screw was operated at a rate of 30 RPM. The automobile spoiler mold was heated to 90°C.

Some of the dried resins for each extruded sample from Tables IX through XI were blow molded using a Rocheleau molding machine equipped with a single-screw extruder. The screw had a 3.81 cm diameter, a length to diameter ratio of 20 and a compression ratio of 2 to 1. Additionally, Sample 5-1 was blow molded into a car spoiler using a Sterling molding machine equipped with a 8.9 cm diameter barrier type screw with a length to diameter ratio of 24:1 and an accumulator of the first-in-first-out design with a capacity of 6.8 kg. The extruder barrel of the blow molding machine was heated and the temperature regulated at 249°C for each of the four

27

temperature zones. The three zones of the accumulator were set at 257°C, 260°C, and 263°C and the die at 265°C. The extruder screw was operated at a rate of 30 RPM. The car spoiler mold was heated to 71°C:

5 The blow molding temperature profile used to produce the blow molded part that appears in Table IX, Sample 9-2, is:

10	<u>Setting</u> <u>Feed</u> <u>Zone</u> <u>(°C)</u>	<u>Setting</u> <u>Transition</u> <u>Zone</u> <u>(°C)</u>	<u>Setting</u> <u>Metering</u> <u>Zone</u> <u>(°C)</u>	<u>Setting</u> <u>Die</u> <u>Zone</u> <u>(°C)</u>
	260	260	270	265
15	<u>Sample</u>	<u>Screw</u> <u>Speed</u> <u>(rpm)</u>		<u>Mold</u> <u>Geometry</u>
	9 - 2	69		Bottle

20

25

30

35

28

Representative blow molding conditions and temperature profiles used to produce the blow molded parts that appear in Table X are:

5	Setting	Setting	Setting	Setting
	Feed	Transition	Metering	Die
	Zone	Zone	Zone	Zone
	(°C)	(°C)	(°C)	(°C)
	240	260	265	260
10				
	<u>Sample</u>	<u>Screw</u>		<u>Mold</u>
		<u>Speed</u>		<u>Geometry</u>
		<u>(rpm)</u>		
	10 - 1	76		Bottle
	10 - 1A	* -		-
	10 - 2	86		Bottle
15	10 - 2A	95		Bottle
	10 - 3	100		Bottle
	10 - 4	84		Bottle
	10 - 5	94		Bottle
	10 - 6	97		Bottle
	10 - 7	93		Bottle
	10 - 8	100		Bottle
20	10 - 9	91		Bottle
	10 - 9A	100		Bottle
	10 - 10	95		Bottle

*Sample not blow molded.

25

30

35

Representative blow molding conditions and temperature profiles used to produce the blow molded parts that appear in Table XI are:

5	<u>Sample</u>	Setting	Setting	Setting	Setting
		Feed	Transition	Metering	Die
		Zone	Zone	Zone	Zone
		(°C)	(°C)	(°C)	(°C)
	11-1 to 11-2	*260	260	260	250
10	11-3 to 11-7	*240	240	245	245

15	<u>Sample</u>	Screw	Mold
		Speed	Geometry
		(rpm)	
	11 - 1	98	Bottle
	11 - 2	77	Bottle
	11 - 3	60	Bottle
20	11 - 4	68	Bottle
	11 - 5	58	Bottle
	11 - 6	47	Bottle
	11 - 7	160	Bottle

* For Samples 11-1 and 11-2, the barrel temperature was inadvertently set too high. Lower settings were used for Samples 11-3 to 11-7. (Higher barrel setting tends to cause more sag of the parison, which becomes very important in making larger objects).

The resins for each Sample in the Tables above were extruded at the designated screw speed through the die to produce a parison. Upon closing the mold, the part is blown with air at about 400 MPa. The blown part is cooled in the mold under pressure and ejected. The mold geometry of the bottles are 22.5 cm high and 7.5 cm diameter; and the

automobile spoilers have dimensions of 136 cm long, 9 cm wide and 1.5 cm thick.

A number of physical properties were measured for each composition. The notch Izod impact strength was determined according to ASTM D-256 measured at 23°C. Tensile properties (tensile yield strength and elongation) at room temperature were measured by ASTM Procedure D-638. The flexural modulus was measured according to ASTM Procedure D-790. Samples were also tested for melt viscosity. The measurement of melt viscosity is described below:

Blow molding resins were first dried in a vacuum oven at 110°C overnight. Melt viscosity was measured using a Kayeness Rheometer under the following test conditions:

Temperature: 270°C and/or 280°C

Die Length to diameter ratio: 20

Die Length: 15.24 mm

Die diameter: 0.76m

Piston diameter: 9.53 mm

Piston rate: 1.52 to 152 mm/minute

In Table I, the inherent viscosities of PET were measured at 25°C according to ASTM Procedure D-2857, "Standard Method for Dilute Solution Viscosity of Polymers". Viscosity was measured using a solution containing 0.5 gm polymer per 100 ml of solution. The solvent used consisted of a mixture of 1 part trifluoroacetic acid and 3 parts methylene chloride by volume.

The inherent viscosity of PBT was measured at 25°C according to ASTM Procedure D-2857, "Standard Method for Dilute Solution Viscosity of Polymers". Viscosity was measured using a solution containing 0.5 gm polymer per 100 ml of solution. The solvent used

consisted of a mixture of 1 part trifluoroacetic acid
and 3 parts methylene chloride by volume. The
polyesters, ethylene copolymer, ionomers, and
additives used in the Samples are defined in the
5 following Tables (I through IV).

In the following samples, all percentages of
component a), b) and c), are given by weight. The
amounts of materials other than components a), b) and
c) are given in parts per 100 parts of the total
10 weight of components a), b) and c). All values
originally obtained in British units have been
converted to S.I. units and rounded, where
appropriate, and finally blanks in the Tables denote
either absence of a particular component or that a
15 particular test was not run.

20

25

30

35

32

Table I

Identification of
Component a)

5	<u>Code</u>		<u>Description</u>
	A	=	Polyethylene terephthalate (PET) containing 0.5 mole percent trimethyl trimellitate branching agent with an inherent viscosity (IV) of 0.65 dl/g.
10	B	=	Recycled bottle resin, linear PET containing about 2 weight percent of comonomer, with an IV of 0.7 dl/g.
	C	=	PET homopolymer with an IV of 1.0 dl/g.
15	D	=	Polybutylene terephthalate (PBT) homopolymer with a melt index of 6.0 - 7.5 gm/10 min. by ASTM D1238 (240°C, 2160 gram weight) having an inherent viscosity of 0.93 dl/g.

20

Table II

Identification of
Component b)

25

Description

Terpolymer of ethylene/27% butyl acrylate/5% glycidyl methacrylate

30

35

Table III

Identification of
Component c)

5	<u>Code</u>	<u>Description</u>
	A	= Sodium ionomer derived from ethylene/15% methacrylic acid copolymer (MAA) in which 59% of the acid groups have been converted to the corresponding sodium salt.
10	B	= Sodium ionomer derived from ethylene/10% MMA copolymer in which 75% of the acid groups have been converted to the corresponding sodium salt.

15

Table IV

Identification of Component d)

20

Description

25 A copolymer prepared by ester interchange followed by polycondensation of 4.52 moles of dimethyl terephthalate, 1.32 moles of dimethyl isophthalate, 1.0 mole of polytetramethyleneether glycol (having a number average molecular weight of 980) and excess 1,4-butanediol in the presence of tetrabutyl titanate catalyst.

30

35

Table V

Identification of Additives

5	<u>Code</u>	<u>Description</u>
	A	Tetrakis [methylene (3,5-di-ter-butyl 4-hydroxyhydrocinnamate)] methane
	B	Oxidized polyethylene used as a mold release agent.
10	C	Acicular naturally occurring calcium meta silicate, surface modified.
	D	Bis (2,4-Di-t-butylphenyl) Pentaerythritol diphosphite
15	E	Zinc ionomer derived from ethylene/10% MAA copolymer in which 71% of the acid groups have been converted to the corresponding zinc salt.

20

25

30

35

35

Samples 6-1 to 6-3 in Table VI, demonstrate the significance of components c) and d) in compositions of the present invention.

Sample 6-1, which is a control Sample
5 contains no component c), the ionomer. Bottles could only be obtained at the very beginning of blow molding (when the screw was only partially filled) on this sample due to the poor processibility, as shown by the fact that the screw speed dropped to zero.

10 Sample 6-2 which contains component c) shows a higher melt viscosity at both 1 sec-1 and 1000 sec-1 than Sample 6-1 but was significantly more processible than Sample 6-1 as shown by the screw speed. Parisons were extruded continuously and blown without
15 difficulty for Sample 6-2.

Sample 6-3 which contains a second polyester, component d, in addition to the ingredients used in Sample 6-2, shows good processibility as evidenced by the high screw speed despite its
20 increased melt viscosity at shear rates of 1 sec-1 and 1000 sec-1 as compared to Sample 6-2. The bottles obtained for Sample 6-3 were smooth inside and outside.

25

30

35

Table VI

Comparison of PET Blow Molding Resins

<u>Sample</u>	<u>ID</u> <u>Comp</u> <u>a</u>	<u>%</u> <u>Comp</u> <u>a</u>	<u>%</u> <u>Comp</u> <u>b</u>	<u>%</u> <u>Comp</u> <u>c</u>	<u>pph</u> <u>Comp</u> <u>d</u>	<u>Additive</u> <u>A(pph)</u>
*6 - 1	A	80.39	19.62	-	-	0.326
6 - 2	A	76.24	18.60	5.15	-	0.206
6 - 3	A	76.24	18.60	5.0	3.0	0.200

<u>Sample</u>	<u>Melt</u> <u>Temp (°C)</u>	<u>RPM</u>	<u>Kg/hr</u>	<u>Viscosity</u> <u>Pa sec @ 1000 sec⁻¹</u>		<u>Viscosity</u> <u>Pa sec @ 1000 sec⁻¹</u>	
				<u>270°C</u>	<u>280°C</u>	<u>270°C</u>	<u>280°C</u>
*6 - 1	324	175	68.1	43917	12599	1303	632
6 - 2	316	175	68.1	56909	19536	1409	900
6 - 3	323	175	68.1	65000	32535	1600	900

36

<u>Sample</u>	<u>Blow</u> <u>Molding</u> <u>(RPM)</u>	<u>Bottle Quality</u>
*6 - 1	45 -- 0	Bottles ruptured in spots; uneven blow in the bottle
6 - 2	65	Strong melt; bottle smooth outside, small specks inside
6 - 3	130	Strong melt; bottle smooth outside and inside

* Control Sample

Sample 7-1 through 7-4 in Table VII show PET compositions of the present invention containing linear PET and branched PET.

5 In comparing Samples 7-1 and 7-3, Sample 7-1 gives bottles with smoother surface than Sample 7-3 which contained no component d and higher levels of ionomer component c).

10 Compare control samples 7-2 and 7-4, which contain no branched PET to Samples 7-1 and 7-3 which contain branched PET. It can be seen that the control samples show lower processibility in the blow molding screw speed.

15

20

25

30

35

Table VII

PET Formulation containing a Branched and Linear PET

<u>Sample</u>	<u>ID</u> <u>Comp</u> <u>a</u>	<u>%</u> <u>Comp</u> <u>a</u>	<u>%</u> <u>Comp</u> <u>b</u>	<u>%</u> <u>Comp</u> <u>c</u>	<u>pph</u> <u>Comp</u> <u>d</u>	<u>Additive</u> <u>A(pph)</u>
7 - 1	A	76.24	18.6	5.17	3.1	0.21
*7 - 2	C	76.24	18.6	5.17	3.1	0.21
7 - 3	A	73.95	18.0	8.02	-	0.20
*7 - 4	C	73.95	18.0	8.02	-	0.20

<u>Sample</u>	<u>Melt</u> <u>Temp</u> (°C)	<u>RPM</u>	<u>Kg/hr</u>	<u>Viscosity</u> <u>Pa sec@1 sec⁻¹</u>	<u>Viscosity</u> <u>Pa sec@1000 sec⁻¹</u>	<u>Viscosity</u> <u>Temp</u> (°C)
7 - 1	305	175	9.2	30045	968	270
*7 - 2	313	175	8.2	26546	1149	270
7 - 3	297	175	9.4	35368	1075	270
*7 - 4	312	175	7.8	41821	1387	270

38

<u>Sample</u>	<u>Flex</u> <u>Mod</u> <u>(MPa)</u>	<u>Blow</u> <u>Molding</u> <u>(RPM)</u>	<u>Bottle Quality</u>
7 - 1	1482	77	Strong melt; very smooth bottle
*7 - 2	1476	40	Parison sagged in mold; bottle surface wavy; some lumps
7 - 3	1462	105	Slight specks on otherwise smooth surface
*7 - 4	1469	47	Parison sagged in mold; bottle surface rough, many lumps

* Control Samples

Sample 8-1 in Table VIII demonstrates the use of branched and linear PET in a composition of the present invention. The melt viscosities at both 1 sec-1 and 1000 sec-1 are excellent and the blow molded automobile spoiler obtained showed very smooth surfaces and excellent melt strength.

10

15

20

25

30

35

Table VIII

Filled Compositions Based on a Mixture of
Branched and Recycled Bottle Linear PET

Sample	ID Comp	% Comp	% Comp	% Comp	pph Comp	Additive A(pph)
	a	a	b	c	d	
8 - 1	A/B	15.2/60.8	17.7	6.25	3.1	0.39

Sample	Additive B(pph)	Additive C(pph)	Melt Temp(°C)	RPM	Viscosity		Viscosity Pa sec@1000 sec ⁻¹
					Kg/hr	Pa sec@1 sec ⁻¹	
8 - 1	0.65	26.0	326	225	90.8	34000	1002

40

Sample Spoiler Quality

8 - 1 Strong melt; spoiler had reasonably smooth surfaces

Samples 9-1 and 9-2 in Table IX illustrate the compositions of the present invention blow molded into automobile spoilers and bottles, respectively.

In particular, the extruded parison had the
5 smooth glossy surfaces and the high melt strength needed for blow molding of large parts with good surface quality.

10

15

20

25

30

35

Table IX

Toughened PBT Blow Molding Composition

<u>Sample</u>	<u>ID</u> <u>Comp</u> <u>(a)</u>	<u>%</u> <u>Comp</u> <u>(a)</u>	<u>%</u> <u>Comp</u> <u>(b)</u>	<u>ID</u> <u>Comp</u> <u>(c)</u>	<u>%</u> <u>Comp</u> <u>(c)</u>	<u>Additive</u> <u>A(pph)</u>
9 - 1	D	78.6	17.2	A	4.3	0.2
9 - 2	D	78.6	17.2	A	4.3	0.2

<u>Sample</u>	<u>Melt Temp</u> <u>°C</u>	<u>RPM</u>	<u>Kg/hr.</u>	<u>Viscosity</u> <u>Pa sec</u> <u>01 sec</u> ⁻¹	<u>Viscosity</u> <u>Pa sec</u> <u>01000 sec</u> ⁻¹
9 - 1	322	200	68.1	38515	1545
9 - 2	322	200	68.1	38515	1545

<u>Sample</u>	<u>Viscosity</u> <u>Temp(°C)</u>	<u>Flex</u> <u>Mod</u> <u>(MPa)</u>	<u>Part Quality</u>
9 - 1	260	1447	Spoilers had smooth glossy surface; parts were impact resistant.
9 - 2	260	1447	Bottles were smooth inside and outside; Excellent melt strength

Samples 5-1 and 5-2 refer to the same blow molding composition but they are distinguished from one another by forming to different parts.

Samples 10-1 through 10-10 in Table X illustrate the compositions of the present invention when component c) contains sodium and/or zinc.

Compare Sample 10-3 to 10-7 and Sample 10-2 to 10-5, these comparisons show that melt viscosity at 1 sec^{-1} increases as the level of component c) is increased. However, when comparing Sample 10-7 to control Sample 10-8 it can be seen that in the presence of sodium ionomer the addition of 0.5% of zinc ionomer had no significant effect on melt viscosity.

Comparison of Sample 10-3 to 10-4 illustrates that in the presence of 5% sodium ionomer, component c), the addition of 0.5 % of a zinc ionomer further enhances melt viscosity at 1 sec^{-1} , however, at the same time, melt viscosity at 1000 sec^{-1} is unchanged, indicating that processibility of the composition is not adversely affected with the improvement in melt strength. Hence, the zinc ionomer while not essential in the present composition had a minor beneficial effect.

25

30

35

Table X

Effect of Sodium and Zinc Ionomers, Component C

Sample	ID Comp (a)	% Comp a	% Comp b	Comp C ID & (%)		Additive D(pph)	Additive A(pph)	Additive E(pph)
				A	B			
10 - 1	D	76.9	18.1	5.0	-	0.3	0.2	-
10 - 1A	D							
10 - 2	D	76.8	18.2	5.1	-	0.3	0.2	0.5
10 - 2A	D							
10 - 3	D	78.9	16.1	5.1	-	0.3	0.2	-
10 - 4	D	78.8	16.2	5.0	-	0.3	0.2	0.5
10 - 5	D	78.9	18.1	3.0	-	0.3	0.2	-
10 - 6	D	78.9	18.2	2.5	-	0.3	0.2	0.5
10 - 7	D	80.9	16.1	3.0	-	0.3	0.2	-
10 - 8	D	80.8	16.2	3.0	-		0.3	0.2 0.5
10 - 9	D	78.8	17.1	4.0	-	0.3	0.2	0.25
10 - 9A	D							
10 - 10	D	78.8	17.1	1.0	3		0.3	0.2 0.25

44

Sample	Melt Temp(°C)	RPM	Kg/hr	Viscosity ⁻¹	
				Pa sec@1sec	Pa sec@1000sec
10 - 1	289	150	68.1	40000	1900
10 - 1A	308	200	68.1	35516	1331
10 - 2	300	150	68.1	43588	1527
10 - 2A	309	200	68.1	39314	1351
10 - 3	294	150	68.1	29109	1451
10 - 4	296	150	68.1	33122	1447
10 - 5	289	150	68.1	22604	1174
10 - 6	289	150	68.1	21545	970
10 - 7	292	150	68.1	18735	1023
10 - 8	290	150	68.1	18074	1011
10 - 9	-	150	68.1	29692	1405
10 - 9A	305	200	68.1	24895	1103
10 - 10	-	150	68.1	26000	1319

Table X cont'd

Effect of Sodium and Zinc Ionomers, Component C

<u>Sample</u>	<u>Bottle Quality</u>	
10 - 1	Tough bottles, smooth surfaces	
10 - 1A	-	
10 - 2	Tough bottles, smooth surfaces,	strong melt
10 - 2A	Tough bottles, smooth surfaces,	strong melt
10 - 3	Tough bottles, smooth surfaces,	strong melt
10 - 4	Tough bottles, smooth surfaces,	strong melt
10 - 5	Tough bottles, smooth surfaces	
10 - 6	Tough bottles, smooth surfaces	
10 - 7	Tough bottles, smooth surfaces	
10 - 8	Tough bottles, smooth surfaces	
10 - 9	Tough bottles, smooth surfaces,	strong melt
10 - 9A	Tough bottles, smooth surfaces,	strong melt
10 - 10	Tough bottles, smooth surfaces,	strong melt

Samples 11-1 through 11-7 in Table VII compare compositions containing zinc and sodium ionomer.

5 Sample 11-1, which is a control Sample, contains no component c). The melt viscosity is low r than Sample 11-2 which contains component c).

Samples 11-1 through 11-4 show an increase in melt viscosity at both 1 sec^{-1} and 1000 sec^{-1} as the level of sodium ionomer increases.

10 Samples 11-2, 11-5 and 11-6 illustrate the increase in melt viscosity at both 1 sec^{-1} and 1000 sec^{-1} as the level of component b) increases.

Comparison of Sample 11-1 and 11-7, illustrate that the use of component c) in Sample 11-7
15 results in the desired increase of melt viscosity. However, melt extrudate of Sample 11-7 is lumpy in contrast to the smooth extrudate of Sample 11-2.

Thus, Table XI shows that component c), A, is superior to Additive C in providing not only high
20 melt strength but substantially improved surface in the extruded parisons.

25

30

35

Table XI

Comparison of Zinc and Sodium Ionomers

Sample	ID Comp (a)	% Comp		ID Comp C	% Comp		Additive		Additive E(pph)
		a	b		C	C	A(%)	E(pph)	
*11 - 1	D	83	17.05	-	-	-	0.2	-	-
11 - 2	D	78	17.05	A	4.26	-	0.2	-	-
11 - 3	D	81	17.05	A	2.00	-	0.2	-	-
11 - 4	D	75	17.05	A	8.00	-	0.2	-	-
11 - 5	D	84	12.0	A	4.26	-	0.2	-	-
11 - 6	D	74	22.0	A	4.26	-	0.2	-	-
*11 - 7	D	82.8	17.05	-	-	-	0.2	0.51	-

Sample	Melt Temp (C)	RPM	Kg/hr	Viscosity -1		Viscosity -1	
				Pa sec@1 sec	Pa sec@1 sec	Pa sec@100 sec	Pa sec@100 sec
*11 - 1	305	150	7.4	7345	-	544	-
11 - 2	307	150	7.5	23000	-	1200	-
11 - 3	298	150	7.9	9500	-	850	-
11 - 4	304	150	8.0	31500	-	1700	-
11 - 5	299	150	7.4	10500	-	1300	-
11 - 6	298	150	7.4	37000	-	1600	-
*11 - 7	297	150	7.5	14230	-	637	-

* Control

Table XI cont'd

Comparison of Zinc and Sodium Ionomers

<u>Sample</u>	<u>Bottle Quality</u>
*11 - 1	Smooth bottles inside and outside
11 - 2	Smooth bottles inside and outside; strong melt
11 - 3	Smooth bottles inside and outside
11 - 4	Smooth bottles inside and outside; strong melt
11 - 5	Smooth bottles inside and outside
11 - 6	Smooth bottles inside and outside; strong melt
*11 - 7	Smooth bottles inside and outside

AD-5881

49

CLAIMS

1. A semi-crystalline blow-moldable polyester composition comprising melt blends consisting essentially of:

- 5 a) 62-88 weight percent at least one poly(ethylene terephthalate) PET selected from the group consisting of branched PET having an inherent viscosity of at least 0.60 dl/g and a mixture of the branched PET
10 with linear PET having an inherent viscosity of at least about 0.65 dl/g, the mixture containing up to 90 weight percent of the linear PET or at least one poly(butylene terephthalate) (PBT) having an inherent
15 viscosity of at least 0.8 dl/g,
 b) 10-30 weight percent of at least one ethylene terpolymer, E/X/Y, where E is ethylene at least 50 weight percent, X is glycidyl methacrylate from 2-10 weight
20 percent and Y is from 0-40 weight percent of a moiety derived from C₁-C₆ alkyl (meth)acrylate,
 c) 2-8 weight percent of at least one ionomer obtained by neutralizing with Na⁺ or
25 K⁺ at least about 40 percent of the carboxyl groups in an ethylene copolymer which contains about 9-20 weight percent of units derived from (meth)acrylic acid and 0-35
30 weight percent of units derived from C₁-C₆ alkyl (meth)acrylate,
the weight percentages given for each of components a), b) and c) being based on the total of these components only.
- 35 2. The composition of Claim 1 containing a further component d), which is at least one polyester

other than PET and is present in the composition in the amount of about 2-6 parts per 100 parts by weight of the composition.

3. The composition of Claim 1 wherein
5 component a) is branched PET.

4. The composition of Claim 1 wherein the linear PET is recycled bottle PET having an inherent viscosity of at least 0.65 dl/g.

5. The composition of Claim 1 wherein
10 component a) is present in an amount of 69-82 weight percent, component b) is present in an amount of 15-25 weight percent and component c) is present in an amount of 3-6 weight percent.

6. The composition of Claim 2 wherein
15 component d) is present in an amount of about 2-4 parts per 100 parts by weight of the total of components a), b) and c).

7. The composition of Claim 5 wherein component b) is an ethylene terpolymer.

8. The composition of Claim 7 wherein
20 component b) is an ethylene terpolymer, where E is ethylene at least 57 weight percent, X is glycidyl methacrylate from 4-8 weight percent and Y is from 10-35 weight percent of at least one moiety derived
25 from C₁-C₆ alkyl (meth)acrylate.

9. The composition of Claim 8 wherein Y is derived from n-butyl acrylate.

10. The composition of Claim 1 wherein component c) is obtained by neutralizing with Na⁺.

11. The composition of Claim 1 which
30 additionally contains up to about 40 parts of at least one filler per 100 parts by weight of the total weight of components a), b) and c).

12. The composition of Claim 11 wherein the filler is selected from chopped glass fibers and acicular calcium metasilicate.

13. The composition of Claim 1 wherein the mixture in component a) contains up to 80 weight percent of a linear PET.

10

15

20

25

30

35

AMENDED CLAIMS

[received by the International Bureau on 21 September 1991 (21.09.91);
original claims 1-13 replaced by amended claims 1-11 (3 pages)]

1. A semi-crystalline extrusion blow-moldable polyester
composition comprising melt blends consisting essentially of:

a) 62-88 weight percent at least one poly(ethylene
terephthalate) PET selected from the group consisting of branched
PET having an inherent viscosity of at least 0.60 dl/g and a mixture of
the branched PET with linear PET having an inherent viscosity of at
least about 0.65 dl/g, the mixture containing up to 90 weight percent
of the linear PET or at least one poly(butylene terephthalate) (PBT)
having an inherent viscosity of at least 0.8 dl/g,

b) 10-30 weight percent of at least one ethylene terpolymer,
E/X/Y, where E is ethylene at least 57 weight percent, X is glycidyl
methacrylate from 4-8 weight percent and Y is from 10-34 weight
percent of a moiety derived from C₁-C₆ alkyl (meth)acrylate,

c) 2-8 weight percent of at least one ionomer obtained by
neutralizing with Na⁺ or K⁺ at least 40 percent of the carboxyl
groups in an ethylene copolymer which contains about 9-20 weight
percent of units derived from (meth)acrylic acid and 0-35 weight
percent of units derived from C₁-C₆ alkyl (meth)acrylate,

the weight percentages given for each of components a), b) and c) being
based on the total of these components only.

2. The composition of Claim 1 containing a further component
d), which is at least one polyester other than PET and is present in the

composition in the amount of about 2-6 parts per 100 parts by weight of the composition.

3. The composition of Claim 1 wherein component a) is branched PET.

5 4. The composition of Claim 1 wherein the linear PET is recycled bottle PET having an inherent viscosity of at least 0.65 dl/g.

5. The composition of Claim 1 wherein component a) is present in an amount of 69-82 weight percent, component b) is present in an amount of 15-25 weight percent and component c) is present in an amount of 3-6 weight percent.

10 6. The composition of Claim 2 wherein component d) is present in an amount of about 2-4 parts per 100 parts by weight of the total of components a), b) and c).

7. The composition of Claim 1 wherein Y is derived from n-butyl acrylate.

15 8. The composition of Claim 1 wherein component c) is obtained by neutralizing with Na^+ .

9. The composition of Claim 1 which additionally contains up to about 40 parts of at least one filler per 100 parts by weight of the total weight of components a), b) and c).

20

25

30

35

10. The composition of Claim 9 wherein the filler is selected from chopped glass fibers and acicular calcium metasilicate.

11. The composition of Claim 1 where in the mixture in component a) contains up to 80 weight percent of a linear PET.

5

10

15

20

25

30

35

INTERNATIONAL SEARCH REPORT

International Application ¹ **PCT/US91/03970**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. (5): C08L 67/02
U.S. CL.: 525/166; 524/456, 513

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System

Classification Symbols

U.S. 525/166; 524/456, 513

Documentation Searched other than Minimum Documentation
to the extent that such documents are included in the fields searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
<u>X</u> Y	US,A, 4,914,152 (MIYASHITA) 03 APRIL 1990 See column 2, lines 53-58, column 5, lines 22-54, lines 63-67 and Example 12.	<u>1,2,4-13</u> 1-13
Y	US,A, 4,753,980 (DEYRUP) 28 JUNE 1988 See column 9, lines 32-37.	9
Y	US,A, 3,673,139 (HRACH) 27 JUNE 1972 See column 2, lines 58-77.	1-13
<u>X</u> Y	JP,A, 59-184,251 (ISHII) 19 OCTOBER 1984 See examples.	<u>1,2,4-13</u> 9

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Δ" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

03 JULY 1991

Date of Mailing of this International Search Report

19 AUG 1991

International Searching Authority

ISA/US

Signature of Authorized Officer

Patricia Sh rt

